45

SPACE GROUP OF 1, 3, 5-TRICHLOROBENZENE

S. G. BISWAS

Optics Department, Indian Association for the Cultivation of Science, Calcutta-32.

(*Received, August* 31, 1959)

Plate IX

ABSTRACT. Debye-Scherrer patterns of pure 1, 3, 5-trichlorobenzene at 30°C as well as at −180°C have been photographed and analysed. Analysis of the patterns shows that the crystals of the substance belong to orthorhombic system with $a=14.15$Å, $b=9.90$Å, $c=6.32$Å and at −180°C only a very small amount of contraction takes place. An electron diffraction pattern of a microcrystal resembling that due to a fibre has also been photographed with the fibre axis along the c-axis of the crystal. The unit cell dimensions mentioned above could explain all the reflections in the electron diffraction pattern.

Considering the dimensions of the unit cell and the approximate density of the crystal the number of molecules in the unit cell was found to be four, the accurate value of the density being 1.34 gm cm^{-3}. The space group D^1_2 has been assigned to the crystal.

INTRODUCTION

The molecules of 1, 3, 5-trichlorobenzene in the vapour state have a three-fold axis of rotation which makes the 0, 0 transition forbidden, and this has been confirmed by the results of the study of ultraviolet absorption spectrum of the vapour (Sponer and Hall, 1948). The 0, 0 band was, however, observed in the absorption spectra of the crystals of the compound at −180°C (Banerjee, 1957) and of its solutions in certain solvents (Roy, 1957). It was pointed out by Banerjee (1957) that the appearance of the 0, 0 band in the spectrum due to the crystals of 1, 3, 5-trichlorobenzene might indicate disappearance of the three-fold symmetry of the molecule in the solid state. More recently the polarisation of the absorption spectra of single crystals of the substance has been studied by Schnepp (1959) and he has observed that the spectrum consists of two parts which are polarised differently and has concluded that the new portion of the spectrum is induced by the crystal field and not by the deterioration of the three-fold symmetry of the molecule. He has also drawn some conclusion regarding the orientation of molecular planes in the crystal. As the crystal structure of the molecule was not known and it is difficult to grow single crystals attempt was made to determine its space group by studying the Debye-Scherrer pattern of the crystal and the results are reported here.

EXPERIMENTAL

To photograph the Debye-Scherrer pattern of 1,3,5-trichlorobenzene the substance was purified by repeated crystallisation from solutions in benzene and ether and only very fine needles were obtained by this method. Different solvents and different processes of crystallisation did not produce any well-defined single crystal. The needles were powdered and packed within a Lindemann glass capillary tube of bore 0.3 mm, and the Debye-Scherrer pattern was photographed at 30°C with a cylindrical camera of radius 4.50 cm. The same pattern was also photographed with the sample at −180°C in the same camera with a special arrangement for producing low temperature (Biswas, 1958). Cu-radiation filtered through nickel foil from a Seifert X-ray tube running at 32KV and 26mA was used to photograph the patterns with an exposure of $3\frac{1}{2}$ hours

The patterns are reproduced in figure 1(a) and figure 1(b) respectively. As well defined single crystals could not be prepared to photograph rotation diagram and to calculate the unit cell dimensions precisely, the habits of the single microcrystals were studied under electron microscope The microcrystals were found to be of fibrous structure and actually an electron diffraction pattern was successfully photographed which closely resembles that due to a fibre (figure 2).

RESULTS AND DISCUSSION

Apart from the difficulty of preparing single crystals the determination of the unit cell dimensions from the powder pattern of 1, 3, 5-trichlorobenzene was found to be very difficult since ordinarily rings due to spacings higher than 4.25 Å could not be observed and therefore rings due to simpler planes from the indices of which the axial lengths of the unit cell could be determined were not recorded. In one of the well exposed photographs, however, very faint rings due to longer spacings were observed. These were extremely helpful in the determination of the unit cell of the crystal.

In the determination of the axial lengths of the unit cell Lipson's (1949) method was applied. First, attempts were made to index the Debye-Scherrer rings in terms of tetragonal and hexagonal systems, but the data did not fit in either of these systems. The unit cell dimensions calculated for the orthorhombic system from the three constants $\lambda^2/4a^2(= .00296)$, $\lambda^2/4b^2(= .00605)$, $\lambda^2/4c^2(= .01482)$ are 14.15, 9.90 and 6.32Å respectively. The spacings observed and the values of $\sin^2\theta$ observed and calculated from the above unit cell dimensions are given in Table 1. It can be easily seen from Table 1 that all the observed spacings of the Debye-Scherrer photograph can be uniquely explained with these unit cell dimensions. It can also be seen from figure 2 that the electron diffraction pattern resembles single crystal rotation photograph. The primitive translation along the fibre axis calculated from the electron diffraction pattern was found to be 6.32Å. This value exactly coincides with the primitive translation along the

TABLE I

Indexing of powder photograph

Observed spacings	Intensity	Values of $\sin^2\theta$ Observed	Values of $\sin^2\theta$ calculated	Indices (hkl)
14.150	(vw)	00300	.00296	(100)
9.900	(vw)	.00605	.00605	(010)
7 071	(vw)	.01186	.01184	(200)
5.327	(vw)	.02086	.02087	(011)
4 963	(vw)	02407	.02383	(111)
			.02420	(020)
4.244	(w)	.03306	.03259	(310)
3.904	(m)	.03890	.03902	(021)
3 769	(vs)	.04175	04198	(121)
3.531	(vs)	04755	.04736	(400)
			.04741	(311)
3.402	(m)		.05086	(221)
			.05074	(320)
3.288	(m)	.05484	05445	(030)
3 093	(w)	06195	.06224	(102)
			.06218	(401)
3.004	(m)	.06569	.06556	(321)
2.780	(m)	.07670	.07717	(212)
2.726	(w)	.07980	.08005	(510)
2.670	(m)	08320	08348	(022)
2.545	(m)	.09150	.09187	(312)
2 490	(m)	09560	.09532	(222)
2 362	(w)	.1063	.1065	(600)
			.1066	(402)
2.300	(m)	.1120	.11162	(041)
			.11269	(412)
2.214	(w)	.1210	.12138	(601)
2 156	(w)	1276	.12743	(611)
2.105	(w)	.1339	.13328	(502)
2.040	(w)	.1424	.14239	(113)
1.959	(m)	.1545	.15421	(150)
1.915	(m)	.1615	.16109	(431)
1.871	(w)	.1695	.16942	(223)
1 768	(w)	.1879	.18944	(800)
1 740	(w)	.1958	.19549	(810)
1.660	(w)	2153	.24137	(333)
1.603	(w)	.2308	.23018	(043)
			.22964	(260)
1.353	(w)	.3238	.32299	(370)
1 332	(w)	.3342	.33392	(044)

TABLE II

Interpretation of electron diffraction photograph

	Observed spacings (Å) and Intensity	Calculated spacings (Å)	Indices (*hkl*)
Zero layer line	1.915 (s)	1.917	(630)
	1.413 (m)	1.414	(750)
	1.155 (m)	1.155	(770)
	0.981 (s)	0.9806	(2,10,0)
First layer line	3.091 (s)	3 086	(401)
	2 156 (s)	2.156	(611)
	1.570 (m)	1.570	(551)
	1.254 (s)	1.252	(761)
	1 055 (m)	1 055	(391)
Second layer line	2.167 (m)	2.172	(232)
	1.631 (vs)	1.631	(252)
	1.311 (m)	1.309	(841)
	1.095 (m)	1.095	(482)
	0.936 (m)	0.9365	(2,10,2)
Third layer line	1.889 (vs)	1.889	(313)
	1 564 (m)	1.564	(243)
	1.293 (m)	1.293	(163)
	1.107 (vs)	1.107	(10,33)
	0.955 (w)	0.9548	(193)
Fourth layer line	1.230 (s)	1.230	(154)
	1.065 (m)	1.065	(844)
	0.955 (m)	0.9548	(384)
			(11,34)
Fifth layer line	1 235 (s)	1.235	(215)
	1 060 (w)	1 060	(525)
	1 016 (w)	1 016	(645)
	0.899 (s)	0 8995	(765)

c-axis obtained from the Debye-Scherrer pattern by applying Lipson's method. Using the values of *a*, *b* and *c* mentioned above all the reflections observed in the electron diffraction pattern could be successfully indexed. The observed spacings and those calculated from the values of *a*, *b*, *c* as well as the indices are given in Table II. As the agreement is satisfactory it can be concluded that the crystal of 1, 3, 5-trichlorobenzene belongs to orthorhombic system with the unit cell dimensions

$$a = 14.15\text{Å}$$

$$b = 9.90\text{Å}$$

$$c = 6.32\text{Å}$$

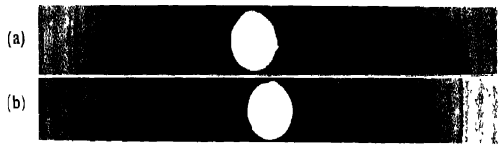

Fig 1 (a) Debye-Scherrer pattern of 1,3,5-trichlorobenzene at 30°C
(b) ,, ,, ,, ,, ,, at −180°C

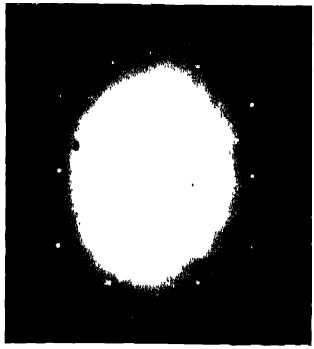

Fig. 2 Electron-diffraction pattern of 1,3,5-trichlorobenzene at 30°C

NUMBER OF MOLECULES PER UNIT CELL

The density of the substance was not found in the existing literature. Attempt was made to measure it and the value found was 1.28 gm cm^{-3}. This does not give any whole number of molecules in the unit cell. If, however, the density is taken as 1.34 gm cm^{-3} the number of molecules per unit cell becomes 4.

the condition of reflection. Since the crystal belongs to orthorhombic system and contains four molecules per unit cell the probable space group is either P_{222}, P_{222_1} or P_{mm2}.

Consideration of the dimensions of the unit cell, the size of the molecule and number of molecules in the unit cell led to the conclusion that the molecules cannot be parallel to any of the axial planes. Hence, the space group P_{222_1} and P_{mm2} are to be excluded.

UNIT CELL DIMENSIONS AT −180°C

The Debye-Scherrer pattern of 1,3,5-trichlorobenzene at −180°C is reproduced in figure 1(b). From the calculation of the spacings of the powder rings it can be easily seen that only very small amount of contraction of the unit cell dimensions takes place at −180°C.

ACKNOWLEDGMENT

The work has been carried out under a scheme financed by the Council of Scientific and Industrial Research. The author's thanks are due to the Council for the Award of a Fellowship. The author is also indebted to Professor S. C. Sirkar, D.Sc., F.N.I., for his kind interest and guidance during the progress of the work.

The author's grateful thanks are also due to Prof. N. N. Das Gupta, Ph.D., of Saha Institute of Nuclear Physics for his kindness in supplying the electron diffraction photograph.

REFERENCES

Banerjee, S. B., 1957, *Ind. J. Phys.*, **31**, 483.
Biswas, S. G., 1958, *Ind. J. Phys.*, **32**, 13.
Lipson, H., 1949, *Acta, Cryst.*, **2**, 43.
Roy, S. B., 1957, *Ind. J. Phys.*, **31**, 588.
Schnepp, O., 1959, *J. Chem., Phys.*, **30**, 863.
Sponer, H. and Hall, M. B., 1948, Contribution a' l'Etude de la Structure Moleculaire, (Deosor, liege), p. 211.